Tetrahedron Letters No.5, pp. 425-428, 1971. Pergamon Press. Printed in Great Britain.

CYCLOADDITIONS OF AMINOISOCYANATES TO HETEROCUMULENES

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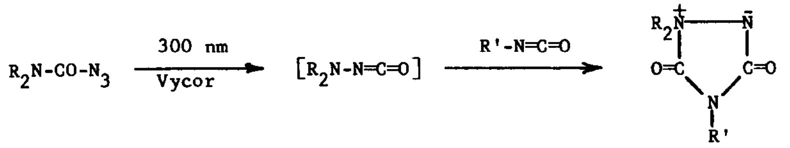
(Received in USA 10 November 1970; received in UK for publication 30 December 1970)

Earlier, we reported the photo-induced Curtius rearrangement of carbamoyl azides in protic solvents [1], and isolation of the products derived from the nucleophilic attack of the solvents on the isocyanate carbonyl of the hypothetical, transient RR'N-N=C=O. We now report that the photolysis of dialkylcarbamoyl azides in aprotic solvents gives transient R_2N-N=C=O in high yields [2]. The aminoisocyanates add to heterocumulenes (including R_2N-N=C=O) to give 1:1 adducts (including dimers). The adducts with isocyanates, R'-N=C=O, are 1,1,4-triazolidin-3,5-dion-1,2-ylides [3,4], as reported first in the independent work of Wadsworth and Emmons [3]. Their and our structure proofs involved (besides elemental analyses, nmr, IR, and mass spectra) the formation of stable hydrochlorides with dry HCl, hydrolysis to give R_2N-NH-CO-NHR' and methanolysis to give R_2N-NH-CO-NR'-COOMe (both by nucleophilic attack on the C=O in position 5), and migration of one of the groups on the ammonium nitrogen to the adjacent N , to give the urazoles IV. In Wadsworth and Emmons' work [3], R is Me and R' is $-NMe_2$, n-butyl, and t-octyl, so that direct comparison of the products was not possible. The isocyanate adducts show two carbonyl stretching

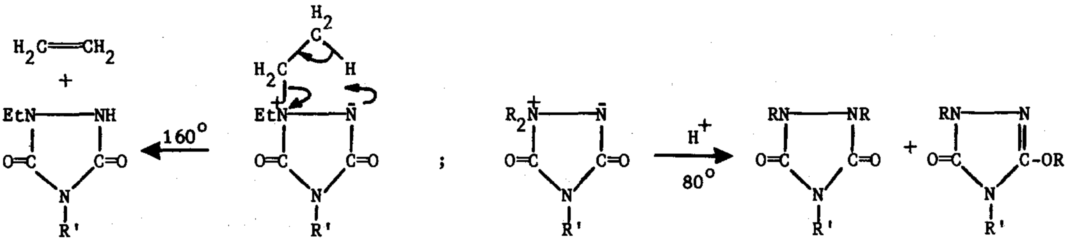


I II III

a : R = Et; R'= NEt_2
b : R = Et; R'= Et
c : R = Et; R'= Me

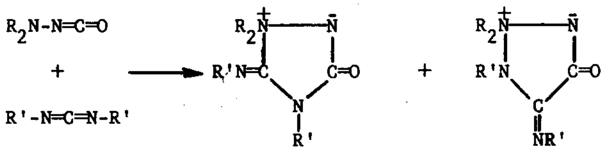
Mp : a = 112-5° (dec.)
b = 81-3°
c = 131-3°

frequencies (e.g. IIIc at 1820 and 1718 cm^{-1}). Catalytic hydrogenation cleaves the $\overset{+}{N}$—$\overset{-}{N}$ bond to give R_2N-CO-NR'-CO-NH_2 (yields : IIIa 70%; IIIb 98%). Pyrolysis of dry III (R = Et) gave ethylene and the 1,4-disubstituted urazoles V (yields : IIIa 91%; IIIb 61%). In solution at 80°, in the presence of acid, IIIb and IIIc are slowly converted to mixtures of the urazoles IV and VI. Presumably, the acid protonates the N^-, removing the inductive stabilization of the R_2N^+ function and rendering it an alkylating agent which then alkylates III on the N^- or the oxygen in conjugation with it. We are studying the mechanism of this process. The structures of the hydrogenation, pyrolysis, and rearrangement products were proved by elemental analyses, nmr, IR, and mass spectra, and by independent synthesis of the hydrogenation products and the urazoles IVb, Vb, and VIb.



Va; Vb IIIa; IIIb IIIb; IIIc IVb; IVc VIb; VIc

The formation of III from an aminoisocyanate and an alkyl isocyanate might be understood in terms of a mechanism involving the attack of the R_2N - nitrogen, acting as a nucleophile, on the sp - carbon of the isocyanate, and the attack of the N^- so created in the alkyl isocyanate moiety on the sp - carbon of the aminoisocyanate [3,4]. However, this mechanism cannot be general (if it operates at all), because the addition of R_2N-N=C=O to carbodiimides gives two adducts (in almost quantitative total yield). One of these, VII, is analogous in structure to III, but the other (VIII), formed in substantial yield, contains a bond between the R_2N - nitrogen of R_2N-N=C=O and one of the nitrogens (rather than the sp - carbon) of the carbodiimide. Nucleophilic attack on a carbodiimide N, putting the negative charge on the sp - carbon, would be most peculiar. We prefer an alternative mechanism in which the aminoisocyanate acts like an allyl anion in a 1,3-dipolar addition. Huisgen [5] has pointed out that the relative orientation of the reaction partners in such additions is not governed by the "1,3-dipole" having a negative and a positive end - addition in two orientations is possible. Photolysis of dialkylcarbamoyl azides in diethyl- and diisopropylcarbodiimides (using light of maximum intensity at 300 nm) gave almost quantitatively mixtures of VII and VIII :

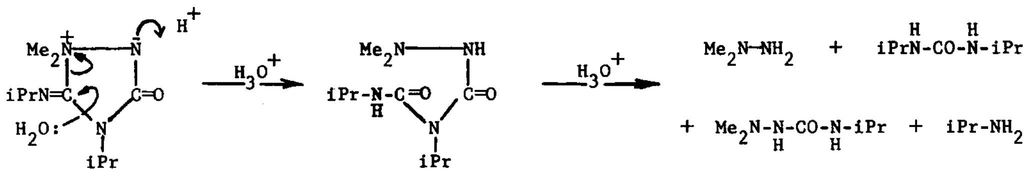


VII VIII

d : R = Me; R' = Et.
e : R = Me; R' = iPr.
f : R = Et; R' = Et.

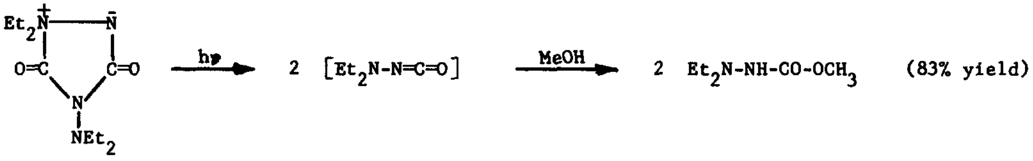
	VII	VII/VIII	VIII
d:	mp 100-2°	3 : 1	oil
e:	mp 141-3°	3 : 2	mp 163-5°
f:	mp 88-9°		not observed

The structures of VII and VIII were determined by elemental analyses, nmr, IR, and mass spectra, and by degradation. In the mass spectrometer, VII readily eliminates R'-N=C=O, while VIII does not. The IR spectrum of VIIe shows a C=N absorption at 1743 cm^{-1}, while VIIIe shows only carbonyl absorption plus C=N absorption around 1662 cm^{-1}. The nmr signal of the $Me_2\overset{+}{N}$ methyls of VIIe is at δ 3.13, due to deshielding by the C=N double bond, while in VIIIe the corresponding signal appears at δ 2.84. Acid hydrolysis of VIIe afforded diisopropyl urea and 4-isopropyl-1,1-dimethylsemicarbazide, identified by comparison with authentic samples. The formation of two further hydrolysis products, 1,1-dimethylhydrazine and isopropylamine, was inferred from comparing the nmr spectrum of a hydrolysis run in HCl/D_2O with that of a HCl/D_2O solution of equimolar quantities of the four hydrolysis products mentioned. The spectra were essentially identical, and we formulate the hydrolysis as :



VIIe

The aminoisocyanate dimer IIIa is stable in refluxing (neutral) methanol (5½ hours reaction time), and its irradiation for 6 hours with 254 nm light in cyclohexene causes only little decomposition. Irradiation for 6 hours in methanol, however, gives a 83% yield of the methanol adduct of the aminoisocyanate - the dimer reverts to the monomer, which can be trapped by methanol, but returns to the dimer in inert solvents.



IIIa

Similarly, the adduct IIIb gives a 75% yield of $Et_2N\text{-}NH\text{-}CO\text{-}OCH_3$ upon irradiation in methanol. Wadsworth and Emmons [3] have reported thermal reversion to isocyanates of their III (R' = t-Oct), but not of their compounds III (such as R' = nBu) which are uncrowded at N-4.

Acknowledgements : We are greatly indebted to the National Science Foundation and to the National Institutes of Health for support of various parts of this work.

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